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STATE-OF-THE-ART FOR THE INORGANIC CHEMICALS INDUSTRY

INORGANIC PESTICIDES

ILLINOIS INSTITUTE OF TECHNOLOGY

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EPA-600/2-74-009a
March 1975

STATE-OF-THE-ART FOR THE INORGANIC CHEMICALS INDUSTRY: INORGANIC PESTICIDES

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ABSTRACT

A literature and field study of the manufacture of inorganic pesticides revealed that many inorganic formulations are still widely used for agricultural purposes. The inorganic pesticide industry is a small but distinct segment of the total agricultural chemical industry. Its manufacturing processes and wastewaters contrast sharply with those associated with organic pesticides. The inorganic pesticide market is dominated by eight products, each of which is discussed in this report with respect to its manufacturing effluent characteristics and applicable pollution control technology. Based upon field studies, it has been demonstrated that five of the eight products can be manufactured without generating any process wastewater. Aqueous effluents from the manufacture of the remaining three inorganic pesticides appear to be directly controllable by previously demonstrated in-plant control and/or wastewater treatment technologies.

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I. CONCLUSIONS

1. The inorganic pesticide industry is a small but distinct segment of the total agricultural chemicals industry.

2. Of the nineteen inorganic pesticides identified in this study, eight dominate the agricultural use market. Sulfur, sodium chlorate and copper sulfate lead these eight.

3. Most inorganic pesticides are manufactured by only two or three companies, often at a single site for each company.

4. Many companies often associated with the sale of inorganic pesticides do not manufacture them, but purchase them in bulk from the primary producers, and repackage under their own label.

5. Several inorganic pesticides of former wide use have declined in popularity, while others continue to be used at previous levels. Included among the former are the mercury chlorides, most inorganic herbicides and calcium arsenate. Sulfur, sodium chlorate, copper sulfate and lead arsenate use has held steady or only slightly declined, while zinc sulfate use has increased in recent years. Zinc sulfate is used primarily as a plant nutrient however, and secondarily as a fungicide.

6. Of the eleven pesticides studied, including the eight major products, there is a manufacturing capability to produce seven of the eleven without any associated wastewater effluent. These seven are arsenic acid, calcium arsenate, copper sulfate, lead arsenate, sodium arsenite, sulfur and zinc sulfate.

7. Of the remaining four products, all had significant wastewaters associated with their manufacture. Sodium chlorate and sodium borate effluents are predominately cooling water. In-plant process modifications can reduce mass pollutant discharges associated with sodium chlorate production by more than 99 percent.

8. Copper carbonate manufacturing wastewaters appear directly treatable by conventional precipitation techniques, with effluent quality equivalent to that achieved by other heavy metal processing industries.

9. Tri-basic copper sulfate wastewater is difficult to treat, due to the complexing nature of the wastewater.

10. In general for the products and plants studied, there appears to be a significant capability for the inorganic pesticide industry to totally eliminate or greatly reduce pollutant discharge.

II. RECOMMENDATIONS

1. Although capabilities exist within the majority of the inorganic pesticide industry to reduce or eliminate pollutant discharge, several problems require further study. Perhaps most critical is the problem of treating metallic wastewaters, such as those associated with tri-basic copper sulfate production. These metals are in a complexed form and cannot be removed by conventional means. This is a problem not only of the inorganic pesticide industry, but also of many other industries having complexed metal wastewaters (11).
2. Another problem area involves the cleanup of reusable shipping containers. Even when process changes eliminate effluent from the manufacture of inorganic pesticides, container cleanup can yield wastewaters containing significant pollutants. In the absence of acceptable cleanup procedures, these containers are frequently stockpiled as a temporary expediency. Guidelines and methodologies for container cleanup are a critical need of the inorganic pesticide industry.
3. This study has revealed no control technology utilized for effluents of sodium chlorate manufacture, other than evaporative ponds. These are applicable, however, only within limited geographical regions. The pollutants associated with sodium chlorate manufacture are not particularly critical insofar as specific contaminants, but fall more into the general and undifferentiated category of dissolved salts (i.e. total dissolved solids). Control of these types of materials is a problem shared by many other industries, and one which has not yet yielded to engineering controls. Further development and demonstration of processes with the potential to control dissolved solids is important.
4. Finally, this study covered only a portion of the total number of inorganic pesticides, although all major products and more than half of all inorganic pesticides identified in the study were investigated. It is probable that some of those not studied, such as ammonium sulfamate, sodium cyanide and cadmium chloride might produce locally significant pollutional sources. Therefore, supplemental study is recommended

to both broaden the information base of the pesticides considered in this study, and expand it to the remainder of the inorganic pesticide industry.

III. INTRODUCTION

In recent years, a great deal of effort has been directed toward identifying and controlling pollution associated with the pesticide industry and the manufacture of its products. As a part of this effort, several studies have been performed to characterize the wastewaters of the industry, and assess the types and levels of treatment technology applicable to those wastewaters (1-6). In recognition of the persistence of organic pesticides in the environment (2,3), and of the trend in the pesticide manufacturing industry to concentrate on organic at the expense of inorganic pesticides (5,6), these studies have essentially been limited to organic pesticides and their associated wastes.

The inorganic pesticide industry is a small but viable segment of the overall industry, and has wastewaters associated with its products which are significant from a pollutional standpoint. These wastes are distinctly different in character and treatability, as compared to wastes of the organic product segment. Further, the inorganic segment may be expected to maintain and perhaps expand its share of the market, as organic pesticide use is increasingly controlled.

Thus a program of wastewater characterization and treatment technology assessment for the inorganic pesticide industry, parallel to that for the organic pesticide industry, is required. As a first step in this effort, this study has been made of the effluents of the major products of the inorganic pesticide industry.

IV. SCOPE OF STUDY

This study represents a preliminary assessment of the pollution potential of the inorganic pesticide industry, the extent of pollution control utilized by that industry, and the data base available within the industry to characterize its wastewaters and effectiveness of pollution control. Primary sources of information included the published literature, those RAPP permit applications received by the EPA for the subject industries at the time of this study, and a limited number of plant visits.

The plant visits included discussions with plant operating personnel, inspection of the manufacturing and treatment facilities, and review of such data on wastewater character and pollution control as were available from the plant. No independent sampling or analyses were undertaken during the study, and data presented within this report were taken only from the previously described sources. Due to the limited scope of the study, relatively few plants could be visited, and selection of plants was based upon an attempt to visit at least one plant manufacturing each significant inorganic pesticide.

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V. DESCRIPTION OF INDUSTRY

Generally, pesticides are classified either on the basis of their chemical nature (e.g. inorganic vs. organic - organophosphorus, chlorinated hydrocarbons, etc.) or according to their use. Table 1 represents a typical "use" classification. On the basis of use, Table 2 lists the inorganic formulations most commonly classified as pesticides (4-7).

In recent years, inorganic compounds have been displaced by organic pesticides in many applications. However, they are still a mainstay of the pesticide industry, representing approximately 20% of the industry's output (4). Prior to 1940, the industry produced essentially only inorganic pesticides. By 1960 the inorganic segment had decreased and stabilized at its present level.

A recent study of the pesticide industry (8) reported a total of 79 inorganic and metallic-organic pesticide products in use. Of these, 28 were mercury-based compounds, 17 arsenic-based, 11 copper-based, 6 other metal-based, and the remainder other inorganic compounds.

Among the inorganic insecticides, the arsenates are most effective and widely used. The lead arsenate commonly used is an acid lead arsenate, $PbHAsO_4$. Calcium arsenate is cheaper than lead arsenate, but its lack of adherence properties renders it less effective. Its use has been greatly reduced by the availability of organic insecticides. The commercial calcium arsenate product is usually a mixture of tricalcium arsenate ($Ca_3(AsO_4)_2$) and lime, called basic calcium arsenate.

Fluorine compounds are stomach-poison insecticides, frequently used as substitutes for the arsenicals. They are extremely poisonous to man and too water-soluble for use on plants, but sodium fluoride is widely employed to control roaches and poultry lice. Sulfur and sulfur compounds are employed to some extent as contact insecticides, but their primary use is as fungicides. The lime sulfurs have been widely used for control of scale insects and to control diseases of tree fruits. The compounds are formed by slaking a dry mixture of lime and sulfur to form among other products, the pentasulfide (7). The use of lime sulfur has declined in favor of organic fungicides, due to its toxicity to plant foliage.

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Table 1. Pesticide Classification on Basis of Use[7]

Insecticides and Miticides
Herbicides
Fungicides and Seed Disinfectants
Rodenticides
Fumigants

Table 2. Principal Inorganic Pesticide Formulations

Insecticides	Calcium Arsenate
	Calcium Cyanide
	Lead Arsenate
	Sodium Cyanide
	Sodium Fluoride
Herbicides	Ammonium Sulfamate
	Arsenic Acid
	Borates
	Magnesium Chlorate
	Potassium Chlorate
	Sodium Arsenite
	Sodium Chlorate
Fungicides	Cadmium Chloride
	Copper Carbonate
	Copper Chloride
	Copper Oxide
	Copper Oxychloride Sulfate
	Copper Sulfate
	Mercuric Chloride
	Mercurous Chloride
	Sodium Polysulfide
	Sulfur
	Zinc Oxide
	Zinc Sulfate

Inorganic sulfur, and compounds of heavy metals, are still widely used as fungicides. Among the inorganic metallic compounds are mercuric and mercurous chloride, which have declined to very limited usage. Elemental sulfur, plus a variety of copper salts, now constitute the bulk of the inorganic fungicide market.

Prior to the introduction of hormone-type weed killers in the early 1940's, the herbicide market was dominated by borate and chlorate compounds, and included potassium and sodium arsenite. Sodium chlorate continues as a major herbicide (non-selective), and another inorganic, ammonium sulfamate has also assumed importance. This is a foliage spray which retards woody growths, but does not effect grassy plants. Although of lesser importance today, the borate compounds and the arsenites continue to hold a small share of the market. Arsenic acid is used (decreasingly)as a defoliant. Use declined by 81% between 1964 and 1966 alone (9), due to reductions in cotton acreage and development of organic substitutes. Since 1962, herbicide production has increased its share of the total pesticide market at an average annual rate of approximately 4% per year. The fungicide share of the market has held essentially constant, while insecticides have decreased insofar as percent of total pesticide production. These trends represent the total (organic plus inorganic) pesticide market.

Trends in Inorganic Pesticide Usage

Herbicide use is becoming more prevalent by farmers, as they increasingly substitute for more expensive mechanical weed control measures (9). Use of inorganic herbicides appears to be rapidly diminishing however, dropping by more then 50 percent between 1964 and 1966. In 1966, inorganic formulations represented only 4 percent of the total herbicide use by farmers.

The inorganic herbicide market is dominated by sodium chlorate, followed by various borate formulations. Borax was among the earliest inorganic herbicides used. The U.S. Department of Agriculture estimates that sodium chlorate pesticidal usage has held essentially constant (at 15,000 tons/yr) since the mid - 1960's, although its relative share of

the market is continually dwindling as more selective weed killers take over (10). Approximately 10 percent of the total U.S. sodium chlorate production is used in agriculture. Other herbicides listed in Table 2 have a very limited market, and like sodium chlorate and the borates, are declining in importance.

Fungicides have been used in agriculture for many years, particularly in fruit and vegetable production. While substantial quantities of fungicides are used by farmers, such use has been relatively constant for some years. There has been a trend of shifting from inorganic to organic forms. One of the earliest effective fungicides was Bordeaux mixture (copper sulfate plus slaked lime), which is still used to a limited extent (9). Many other inorganic products were later found to be effective fungicides, including sulfur, and copper salts. Mercuric and mercurous chlorides, as well as organo-mercury compounds, proved to be particularly effective fungicides, although their use declined rapidly from 1967 (Figure 1).

Among the inorganic heavy metal fungicides in current use, copper sulfate predominates. It is widely used on citrus crops, among others, with these citrus crops representing 64 percent of the total domestic copper sulfate fungicide use in 1966 (9). However, copper sulfate represented (on a tonnage basis) only 27 percent of the total inorganic copper salts used as fungicides in that year, and 22.6 percent of the total inorganic fungicide use (excluding sulfur). Other copper salts include the oxychloride sulfate, carbonate, oxide and chloride. No information is available on the relative significance of these latter copper salts, although there is some evidence from this study that copper oxychloride sulfate may be among the more important.

Of the total domestic usage of copper sulfate, approximately 40 percent is used in agriculture (Figure 2), with 31.1 million pounds used in 1971 (10). An estimated 60 percent of the agricultural copper sulfate is used as a fungicide, 20-25 percent as an algacide, 10-15 percent as an animal nutrient and 4-5 percent as a plant trace nutrient (10). For the ten year period 1962-1971, agricultural copper sulfate use has held fairly constant, as shown in Figure 3.

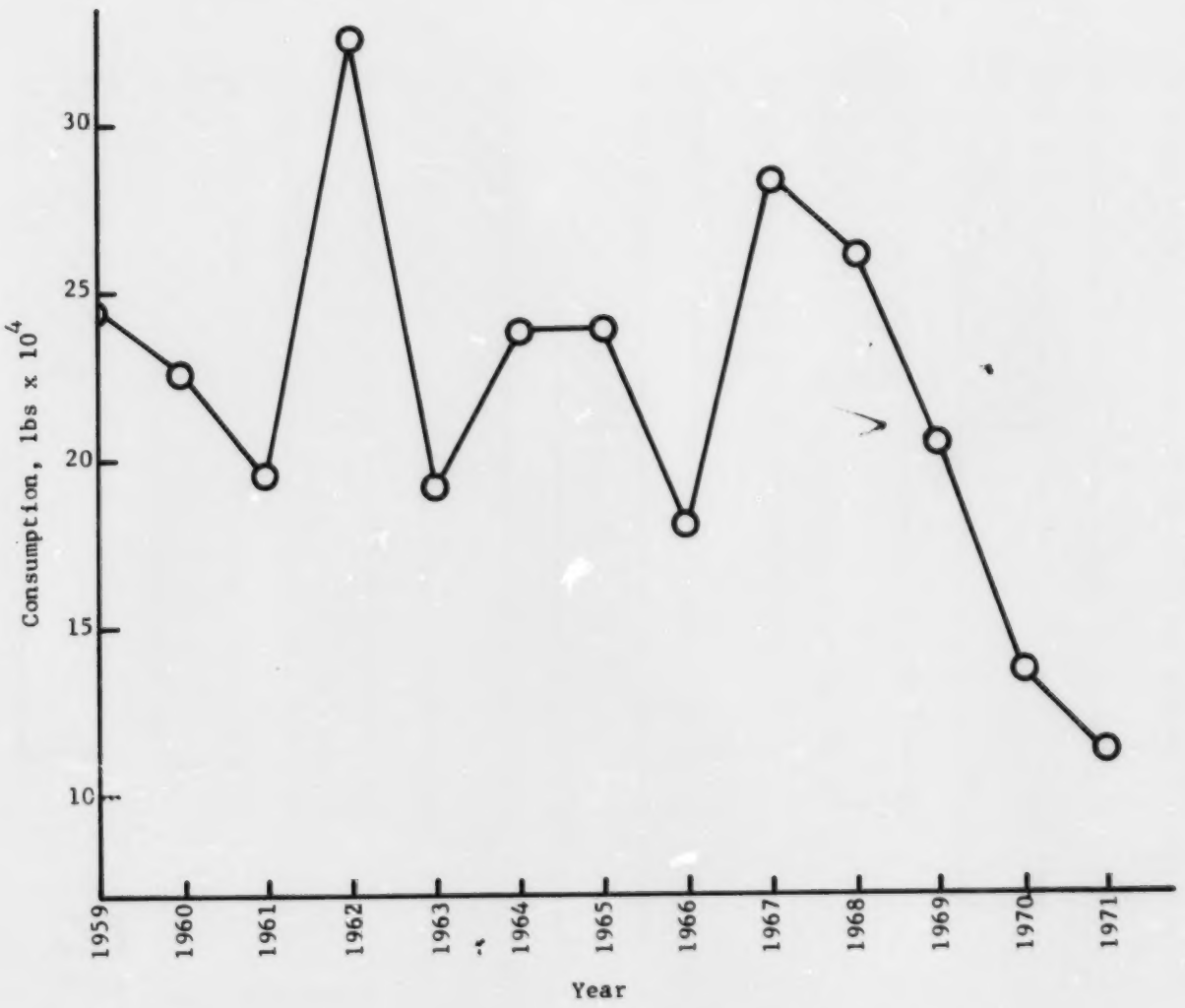

Figure 1. Annual Mercury Usage in Pesticide Manufacture (10)

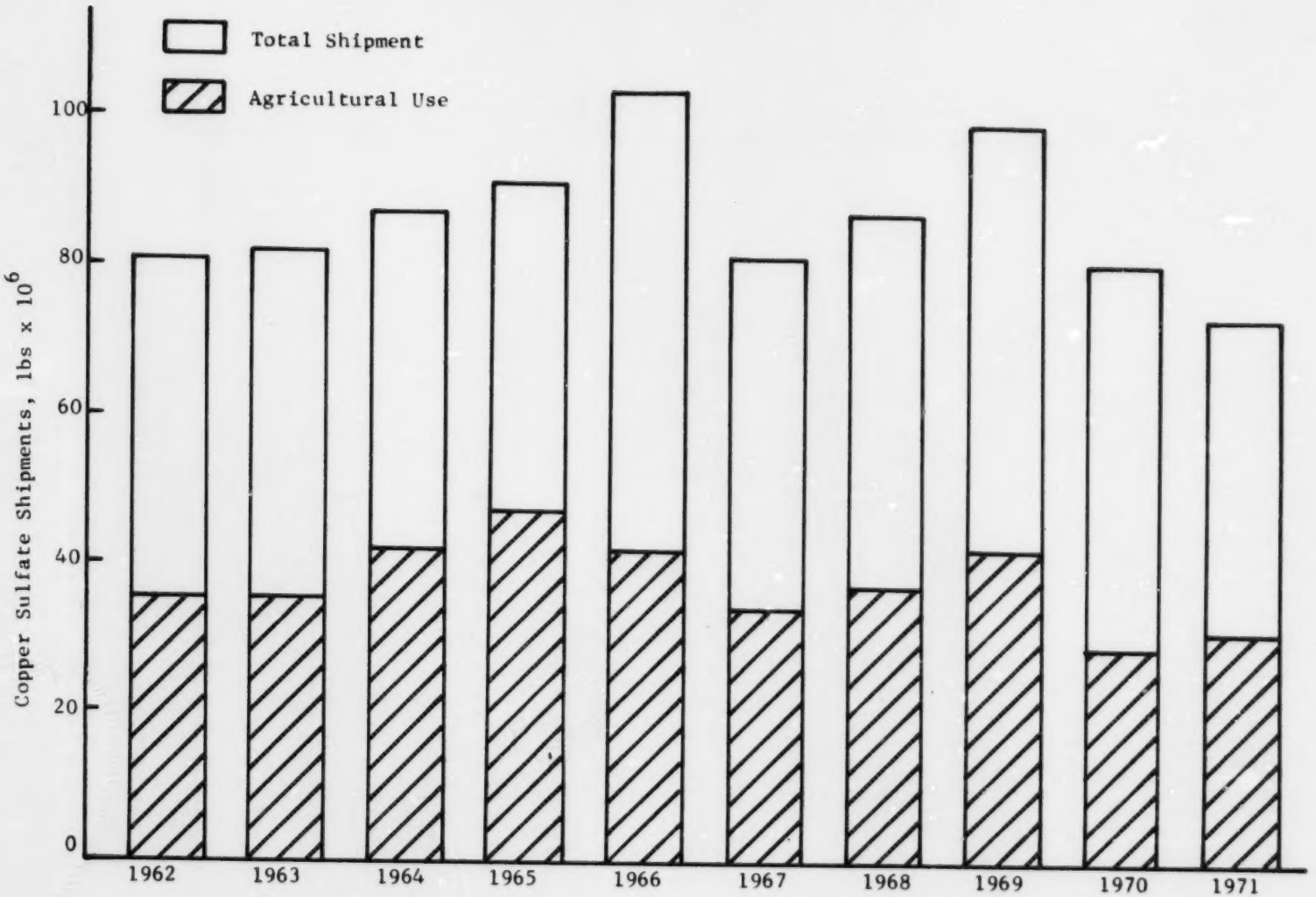

Figure 2. Annual Domestic Shipments of Copper Sulfate (10)

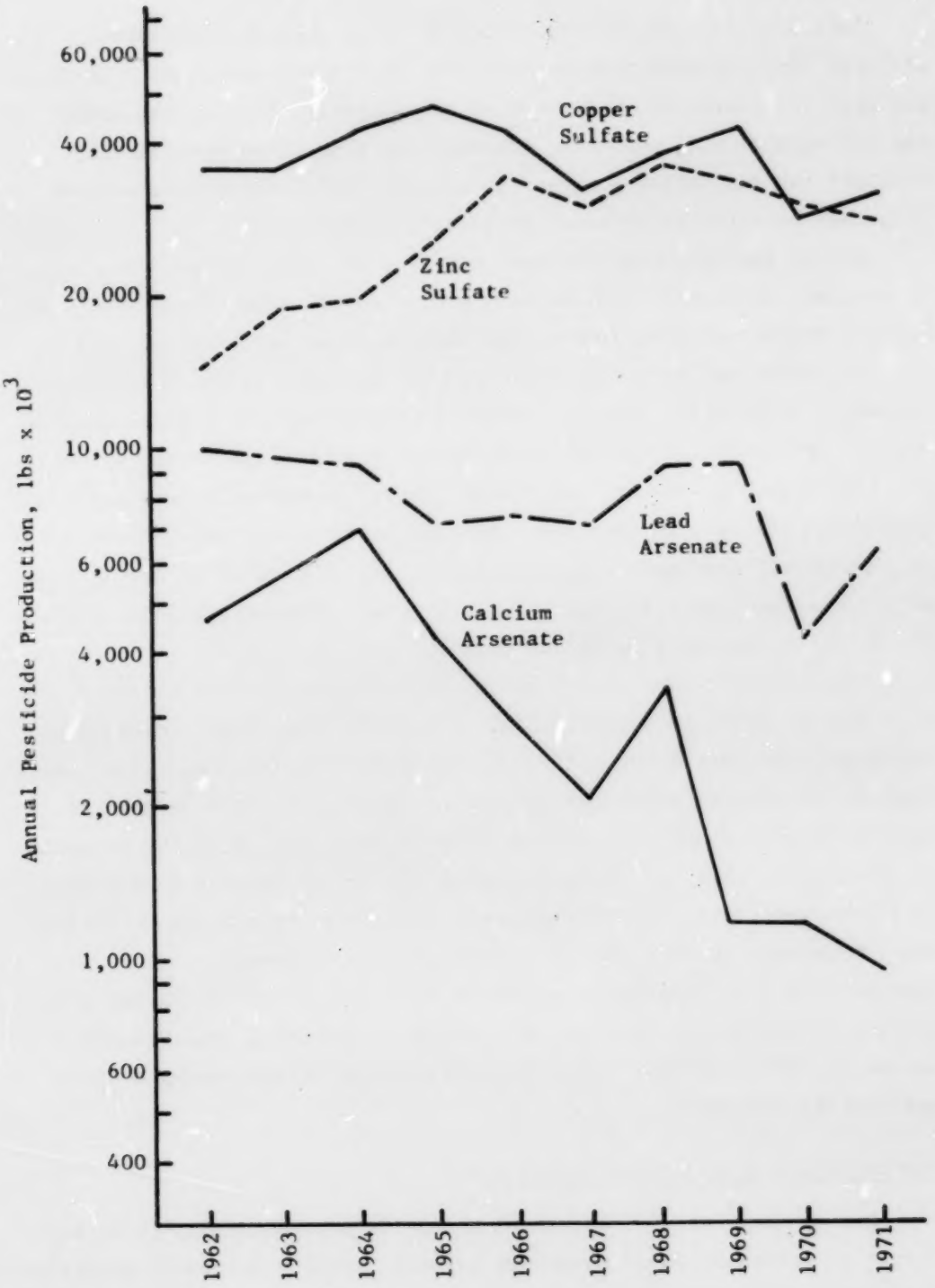

Figure 3. Annual Inorganic Pesticide Production (4, 10)

Both zinc sulfate and zinc oxide are also used as fungicides, although their primary agricultural use areas plant nutrients. During the past ten years, 30-40 percent of the domestic zinc sulfate usage was for agricultural purposes, although the proportion specifically utilized for fungicidal purposes is unknown (10). Total agricultural usage has been fairly constant (Figure 3), since 1965.

Sulfur has long been the most widely used fungicide product, accounting for nearly twice as many pounds as all other fungicides combined. Sulfur has been widely used (87% of total agricultural sulfur use) on peanut and deciduous fruit crops, although its use has declined somewhat due to short supply, price increases and the availability of organic substitutes. Current estimates of sulfur usage as a fungicide are 150 million pounds per year (10). This is comparable to the 137 million pounds used in 1964 (9). In that year, sulfur constituted 93 percent of all inorganic fungicide usage, and 82 percent of all inorganic pesticides used, on a tonnage basis. It thus represents a major portion of the total inorganic pesticide market.

The inorganic insecticide market is dominated by lead arsenate, with calcium arsenate a poor second (Figure 3). Inorganic insecticides represent less then 5 percent of the total insecticide usage (9). Lead arsenate is particularly used in apple orchards, and it's market has held relatively stable for several years (Figure 3). With the exception of 1970, it's usage has increased since 1965 at an average annual rate of 3.2 percent (10). Calcium arsenate production is rapidly declining, down 56 percent in 1971 over the previous 5-year average. However, the U.S. Department of Agriculture reports the declining production is matched by declines in stockpiles, and that agricultural demand is fairly steady. Other inorganic insecticides occupy a minor position in the market.

Manufacturers of Inorganic Pesticides

Due to the sensitive nature of pesticide manufacturing, it is difficult to determine which companies actually produce inorganic pesticides and which merely purchase in bulk and repackage under their own label.

After identifying which inorganic products were utilized for pesticidal purposes (Table 2), a detailed search was made of chemical producer directories and manufacturing catalogs, such as the Stanford Research Institute "Directory of Chemical Producers" (1972), to identify suppliers of chemicals falling into the inorganic pesticide category. Since many of the inorganic compounds have uses other than as pesticides, not all manufacturers are actually pesticide sellers, per se. For example, sodium chlorate is used in the metallurgical, textile, dye and pulp and paper industries, as well as for an agricultural herbicide.

As a result of the review of chemical product directories, plus discussions with the Manufacturing Chemists Association and National Agricultural Chemicals Association, fifty companies were tentatively identified as producing inorganic chemicals for pesticidal use. Each of these companies was contacted to determine if they did produce the particular inorganic chemical, and if they sold it as a pesticide. Of the fifty companies contacted (Appendix A), twenty responded in the affirmative, that they did produce and market inorganic pesticides. These twenty, and their pesticide products, are listed in Table 3.

The remaining thirty companies either did not produce the chemicals, produced them but did not merchandise them as pesticides, or purchased pesticide in bulk from the twenty primary manufacturers and repackaged under their own label. This latter category included several of the larger companies frequently identified as major pesticide manufacturers. Inorganic pesticides listed in Table 2, for which producers were not identified, include

sodium fluoride
ammonium sulfamate
potassium chlorate
zinc oxide
sodium cyanide.

With the exception of zinc oxide, whose primary agricultural use is as a plant nutrient, and possibly ammonium sulfamate, these five compounds are very minor insofar as their agricultural and/or pesticidal use and

Table 3. Producers of Inorganic Pesticides

Company	Arsenic Acid	Borate Compounds	Cadmium Chloride	Calcium Arsenate	Calcium Cyanide	Copper Carbonate	Copper Chloride	Copper Oxide	Copper Oxychloride Sulfate	Copper Sulfate	Copper Sulfate (Tri-Base)	Lead Arsenate	Magnesium Chlorate	Mercury Chlorides	Sodium Arsenite	Sodium Chlorate	Sodium Polysulfide	Sulfur	Zinc Sulfate
Allied Chemical Corp.	X			X											X				
American Cyanamid Co.					X														
Chemetron Corp.							X												
Chevron Chem. Co.				X						X		X			X				
Cities Service Co.						X				X	X								
FMC Corporation							X					X					X	X	
Harshaw Chem. Co.							X												
Hooker Electrochem. Co.																	X		
Kerr-McGee Chem. Co.		X						X			X						X		
Los Angeles Chem. Co.	X			X					X			X				X			

Table 3. (Continued)

Company	Arsenic Acid	Borate Compounds	Cadmium Chloride	Calcium Arsenate	Calcium Cyanide	Copper Carbonate	Copper Chloride	Copper Oxide	Copper Oxychloride Sulfate	Copper Sulfate	Copper Sulfate (Tri-Base)	Lead Arsenate	Magnesium Chlorate	Mercury Chlorides	Sodium Arsenite	Sodium Chlorate	Sodium Polysulfide	Sulfur	Zinc Sulfate
Pennwalt Corp.	X												X			X			
Phelps Dodge										X									
So. Calif. Chem. Co.							X	X	X	X									X
Stauffer Chem. Co.																		X	
U.S. Borax		X																	
Van Water & Rogers										X									
Ventron Corp.														X					
Volunteer Purch. Group	X																		
W. A. Cleary Corp.			X																
Woolfolk Chem. Works				X								X			X				

as such constitute only a small fraction of the pesticide market.

Many of the companies identified in Table 3 have plants at several locations. Plants, products and locations are given in Table 4, and their geographical distribution shown in Figure 4. With the exception of those plants concentrated in California, the facilities are fairly evenly distributed throughout the north, north central and southern sections of the country. Distribution, to a large extent, appears to be influenced more by the product market (ie. agriculture) then other factors, although a few are located adjacent to sources of their raw materials. One example is the Cities Services plant in Copperhill, Tennessee, located near copper mines owned and operated by that company.

In general, the plants fall into two categories: (1) those in which pesticide production represents only a portion of the total production and, (2) those facilities devoted solely to pesticide manufacture. Plants in the first category either produce other chemicals not marketed as pesticides, or only a portion of the pesticidal-type chemicals are sold for pesticide use; the remainder being marketed for other purposes. Examples are the plants manufacturing sodium chlorate, copper sulfate and similar compounds of wide general industrial application.

The inorganic pesticide industry is a small and readily identified segment of the total industry, typically consisting of one or a few plants within each company which produce inorganic pesticides. Although not previously well characterized as to pollutional impact, it is by nature an industry which is amenable to direct study.

TABLE 4. Producers of Inorganic Pesticides

Company	Plant Location	Products
1. Allied Chemical Corp.	Baltimore, Maryland	Arsenic acid Calcium arsenate Sodium arsenite
2. American Cyanamid Co.	Linden, New Jersey	Calcium cyanide
3. Chemetron Corp.	Cleveland, Ohio	Copper chloride
4. Chevron Chemical Co.	Maryland Heights, Missouri Richmond California	Sodium arsenite Calcium arsenate Copper sulfate Lead arsenate
5. Cities Service Co.	Copperhill, Tennessee	Copper carbonate Copper sulfate Tri-basic copper sulfate
6. FMC Corporation	Middleport, New York Richmond, California Modesto, California Fresno, California Jacksonville, Florida Richmond, California	Lead arsenate Copper chloride Sodium polysulfide Sulfur Sulfur Sulfur
7. Harshaw Chemical Co.	Elyria, Ohio	Copper chloride
8. Hooker Electrochemical Co.	Niagara Falls, New York Columbus, Mississippi Taft, Louisiana	Sodium chlorate Sodium chlorate Sodium chlorate

TABLE 4. (continued)

Company	Plant Location	Products
9. Kerr-McGee Chemical Corp.	Henderson, Nevada	Sodium chlorate
	Hamilton, Mississippi	Sodium chlorate
	Powder Springs, Georgia	Tri-basic copper sulfate
		Copper oxide
	Trona, California	Borax
		Pentahydrate borax
		Sodium pentaborate
10. Los Angeles Chemical Co.	South Gate, California	Arsenic acid
		Calcium arsenate
		Copper oxychloride sulfate
		Lead arsenate
		Sodium arsenite
11. Pennwalt Corp.	Portland, Oregon	Magnesium chlorate
		Sodium chlorate
	Bryan, Texas	Arsenic acid
12. Phelps Dodge	Laurel Hill, New York	Copper sulfate
	El Paso, Texas	Copper sulfate
13. Southern California Chemical Co.	Los Angeles, California	Copper sulfate
		Copper chloride
		Copper oxychloride sulfate
		Copper oxide
		Zinc sulfate
14. Stauffer Chemical Co.	Compton, California	Sulfur
	Dayton, New Jersey	Sulfur
	N. Portland, Oregon	Sulfur
	Richmond, California	Sulfur
	Tampa, Florida	Sulfur

TABLE 4. (continued)

Company	Plant Location	Products
15. U.S. Borax Co.	Columbus, Mississippi Wilmington, California Boron, California	Sodium metaborate Polybor chlorate Sodium tetraborate
16. Van Water & Rogers	Midvale, Utah Wallace, Idaho Metaline Falls, Idaho	Copper sulfate Copper sulfate Copper sulfate
17. Ventron Corp.	Woodridge, New Jersey	Mercuric chloride Mercurous chloride
18. Volunteer Purch. Groups	Bonham, Texas	Arsenic acid
19. W. A. Cleary Corp.	New Burnswick, New Jersey	Cadmium chloride
20. Woolfolk Chemical Works	Ft. Valley, Georgia	Calcium arsenate Lead arsenate Sodium arsenite Zinc sulfate

Figure 4. Geographical Distribution of Inorganic Pesticide Manufacturing Facilities

VI. DESCRIPTION OF WASTE CHARACTER

Information on the nature of wastewaters associated with manufacture of inorganic pesticides was initially assessed as being available from (1) published literature, (2) RAPP discharge permit applications, and (3) direct contact with the manufacturers by plant visits. An intensive search of the literature failed to reveal any wastewater characterization or treatment reports specifically pertaining to the subject industry. In light of subsequently developed information revealing the limited nature of the industry, this absence of published data is not surprising. The only published references to wastewaters were contained in reports of two plant visits previously undertaken by contractors to EPA, and neither report included quantitative data. These reports were for a mercury chloride plant (5), and a sulfur facility (6).

Somewhat better success was encountered in reviewing permit applications. Several applications were available for plants which produced inorganic pesticidal chemicals, and limited information within this report was extracted from those applications. However, many plants which produce only inorganic pesticides have not submitted permit applications, because they have no discharge or possibly because they discharge to municipal facilities. Most plants for which applications were available were larger facilities, only partially devoted to inorganic pesticide manufacture. The reliability of data from these applications is questionable, since in most cases the effluents represented combined discharges for both inorganic pesticide plus other product lines.

In recognition of the limited information available, other than through direct plant visits, six plants were selected to visit on the basis of products manufactured. In order to assess which products were most significant, major inorganic pesticides were listed in decreasing tonnage of usage and total market value, as shown in Table 5. Tonnage rank is based upon values previously reported in Chapter V. The market value ranking, although somewhat outdated, is generally comparable to the current tonnage ranking.

Table 5. Ranking of Major Inorganic Pesticides

Pesticide	Tonnage Rank	Market Value Rank (7)
Sulfur	1	1
Sodium Chlorate	2	3
Copper Sulfate	3	2
Zinc Sulfate	4	6
Sodium Borates	5 (est.)	5
Lead Arsenate	6	4
Calcium Arsenate	7	8
Sodium Arsenite	8	7

Table 6. Inorganic Pesticide Products of Plants Visited

Arsenic Acid	Lead Arsenate
Calcium Arsenate	Sodium Arsenite
Copper Carbonate	Sodium Chlorate
Copper Sulfate	Sodium Borates
Copper Sulfate, Tri-basic	Sulfur
	Zinc Sulfate

Table 6 lists products produced by those six plants visited. The products include all listed in Table 5, plus arsenic acid and copper carbonate, and incompass more than half of the products listed in Table 3. Of six plants visited, four had submitted discharge permit applications, and two had no process wastewater discharge. The six plants visited (insofar as the ten products investigated) appear to employ average to excellent production and wastewater control technology. The manufacture, wastewater character and treatment technology employed for each product is described in the following sections.

Arsenic Acid

At the plant visited, arsenic acid is produced on a batch basis, as an intermediate in the manufacture of arsenate pesticides. A schematic of the arsenic acid manufacturing process is shown in Figure 5. Nitric acid is mixed with arsenic trioxide to form arsenic acid. Unspent nitric acid is recovered. Arsenic acid is stored, to be utilized in the manufacture of calcium and lead arsenate. The arsenic acid reaction produces nitrous oxide fumes, which are scrubbed in a raschig ring packed tower, with countercurrent (recycled) water flow. The water is returned to a storage tank, where a portion is employed for processing and vat cleanup. The remainder is reused in the NO_x scrubber tower. The portions used for processing and vat cleanup are evaporated to dryness in rotary gas-fired driers, to recover product. There is thus no wastewater associated with this process.

Calcium Arsenate

Both calcium and lead arsenate are produced by similar reaction processes. Lime or lead oxide is mixed with arsenic acid to produce calcium or lead arsenate, respectively (Figure 6). The products are piped to drum driers. Water vapor from the driers is collected and vented to stacks. Cleanup water from the batch mix vats is either saved to mix with the next batch, or evaporated in the drum driers to recover product. All product spills are caught in spill-pans below each processing unit. Spilled liquids are recycled back to the processing line. There is thus

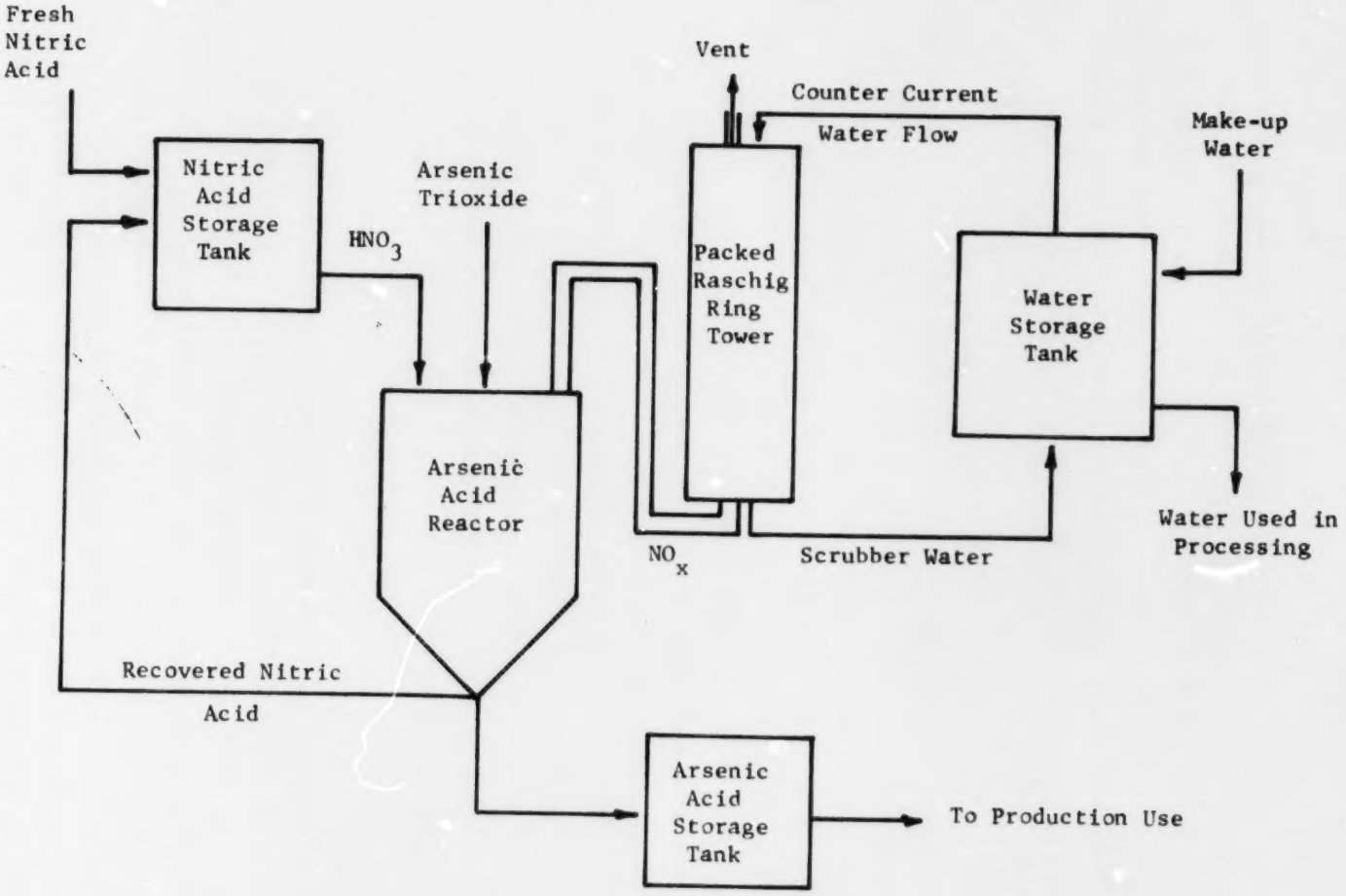

Figure 5. Arsenic Acid Production

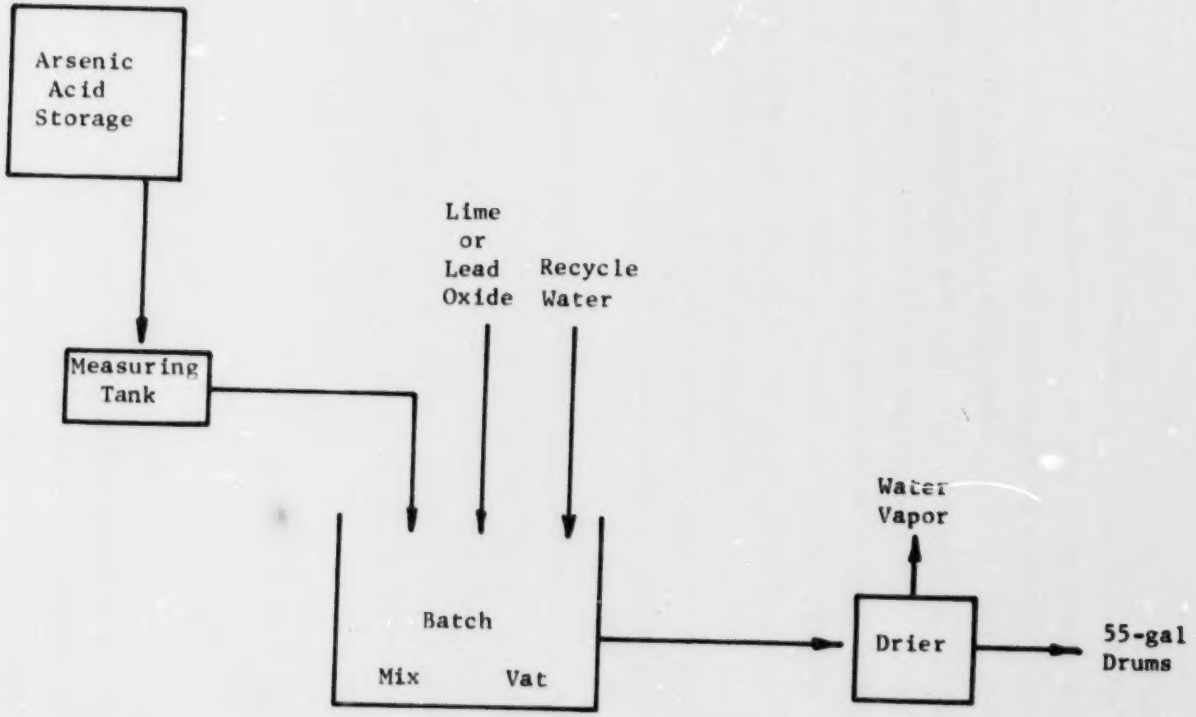

Figure 6. Production of Lead and Calcium Arsenate

no wastewater associated with the manufacture of either calcium or lead arsenate at this plant.

Copper Carbonate

Copper shot is reacted on a batch basis with steam-heated sulfuric acid, to form a concentrated copper sulfate solution. To manufacture copper carbonate, soda-ash is mixed with the copper sulfate concentrate in a batch reactor. Lime is then added to neutralize the mix to pH 6.3-6.5, thereby precipitating copper carbonate. The precipitate is settled, vacuum filtered and dried. The supernatant from the precipitation tank, and the filtrate are discharged as wastewater. Average wastewater flow is approximately 11,000 gallons per ton of copper carbonate product. Of this, approximately 7,000 gallons is vacuum filter wash and water pump flow. Table 7 presents wastewater characteristics and pollutant discharge from the copper carbonate manufacturing process. The metals, aside from copper, shown in Table 7 represent impurities in the copper shot employed in the process.

Currently, discharge is to a holding pond and thence into a nearby waterway. Plans are presently being formulated, in cooperation with the appropriate state regulatory agency, to design and construct a precipitation treatment plant to remove copper and other heavy metals from the wastewater. This will also likely include provision for reductions in suspended solids.

Copper Sulfate

Copper shot is reacted on a batch basis with steam-heated sulfuric acid to form a supersaturated copper sulfate solution. When the solution is allowed to cool, copper sulfate crystals form. The supernatant "mother liquor" is decanted and either reused for the next batch of copper sulfate crystals, or used in the production of tri-basic copper sulfate or copper carbonate. Any washwater used in cleanup is retained in the crystallization vats, and used in the copper sulfate production process. Steam to heat the solution is produced on site, from chemically softened creek water. Sludge from the softening process, plus boiler

Table 7. Effluent Characteristics from Copper Carbonate Production

Parameter	Concentration, mg/l*	Discharge, lbs/ton Product
pH	6.3-6.5	--
Copper	13	1.21
Iron	3.6	0.33
Magnesium	1.0	0.09
Manganese	0.1	0.01
Nickel	0.1	0.01
Lead	0.7	0.06
Zinc	1.3	0.12
Chromate	<0.5	< 0.05
Sulfate	NA	NA
Chloride	16	1.48
NH_3-N	10	0.93
Diss. Solids	36,650	3,398
Susp. Solids	59	5.47

*except pH

blowdown, constitute the only wastewaters associated with the copper sulfate process. These are discharged directly to a holding pond, where the sludge settles. Pond overflow is to an adjacent waterway.

Copper Sulfate, Tri-basic (TBCS)

Production involves addition of 10 percent ammonium hydroxide solution to copper sulfate mother liquor. Lime is added to adjust the pH to 6.3-6.5, with TBCS precipitating from solution. The settled precipitate is vacuum filtered and dried. The supernatant from the precipitation vat, and the filtrate are discharged as wastewater. Average wastewater flow, including vacuum filter flow, is approximately 7,000 gallons per ton of product. Of this, approximately 50 percent is filter backwash and water pump effluent.

Table 8 presents effluent data from the TBCS production line. The

Table 8. Effluent Characteristics of TBCS Production

Parameter	Concentration, mg/l*			Discharge
	minimum	average	maximum	ave. lbs/ton product
pH	5.9	6.4	7.0	--
Copper	131	136	150	7.77
Iron	4.9	38	84	2.17
Magnesium	0.8	1.5	2.2	0.09
Manganese	0.05	0.17	0.20	0.01
Nickel	0.1	0.9	2.5	0.05
Lead	--	0.12	--	0.01
Zinc	1.3	1.4	1.7	0.08
Chromate	<0.3	<0.4	<0.5	<0.02
Chloride	2.5	3.4	5.5	0.19
Sulfate		24,000		1,371
NH_3-N	3,840	4,800		274
Diss.Solids		35,400		2,023
Susp.Solids	14	240	814	13.71

*except pH

effluent is high in ammonia, which acts to complex metals and hold them in solution. For this reason, the wastewater contains higher levels of metals than would be normal for the pH shown. Except for copper, the effluent metals shown in Table 8 represent impurities in the copper shot used to form the copper sulfate solution. Due to the ammonia complexes formed, simple precipitation treatment is not expected to be effective for this wastewater, insofar as heavy metals removal, and the plant is currently evaluating means to either substitute other raw materials for the ammonia hydroxide, or strip ammonia from the wastewater prior to precipitation treatment.

Lead Arsenate

Lead arsenate is manufactured by a batch process, similar to that previously discussed for calcium arsenate (see Figure 6). Lead oxide is mixed with arsenic acid on a batch basis. The precipitate slurry is drum dried and packaged. Water vapors are collected and vented, and all spills are caught and returned to the process. At the particular plant visited, there are thus no wastewaters associated with lead arsenate production. However, it has been reported that other producers of lead arsenate filter the precipitate slurry prior to drying, to remove undesirable (soluble) reaction side products. For those producers, this filtrate liquid may require treatment prior to discharge, for removal of lead and arsenate.

Sodium Arsenite

Sodium arsenite is manufactured as a liquid product, by batch mixing caustic, water and arsenic trioxide. The product is sold in the liquid form, and there is thus no liquid waste associated with the process. All cleanup water from the batch mix vats is saved to mix with the next batch.

Sodium Chlorate

Two sodium chlorate manufacturing facilities were visited, and the following discussion represents the processes used by both. Difference

in processing between the two plants are indicated. Additional effluent data from the RAPP permit application of a third plant is included in the discussion of wastewater character.

Sodium chlorate production basically involves electrolysis of concentrated sodium chloride solution to produce a mixture of sodium chlorate, sodium hypochlorite and residual sodium chloride. As shown in Figure 7, rock salt plus makeup water is added to a "mother liquor" representing recycled electrolyte solution from which sodium chlorate has been crystallized. The brine solution is decanted to the electrolytic cells. At one plant, muriatic acid is added for pH control, and sodium dichromate to improve cell efficiency. The cells are cooled by a once-through non-contact water flow. After completion of electrolysis, the sodium chlorate "mother liquor" is decanted to a hypochlorite decay tank, where (at one plant) barium chloride is added to precipitate (as barium sulfate) sulfate impurities in the mother liquor. The solution is then pumped to a precipitation tank, where soda-ash is added. This precipitates calcium as $CaCO_3$, and excess barium as $BaCO_3$. At the second plant, sulfate impurity in the sodium chloride is removed by lime addition to the mother liquor to precipitate calcium sulfate, with residual calcium precipitated as calcium carbonate by addition of soda-ash. In both plants, the solution is then pressure filtered to remove the mixture of precipitates previously formed, plus graphite fragments from the cell electrodes. The pressure filter is backwashed several times daily, with cooling water, and the backwash discharged.

At one plant, the filtrate then goes to a steam heated evaporator, to drive off water vapor and precipitate NaCl. The sodium chlorate-rich supernatant is decanted to a chlorate crystallization process, while the NaCl slurry is vacuum filtered. Crystalline NaCl is returned to the dissolver, and filtrate pumped to the chlorate crystallizer. The chlorate solution is cooled by refrigeration, or by reducing the pressure, with water vapor released. This vapor, plus that driven off in the steam heated NaCl crystallization chamber is condensed using cooling water at 2,500 gpm, and returned to the dissolver, along with a portion of the cooling water for makeup.

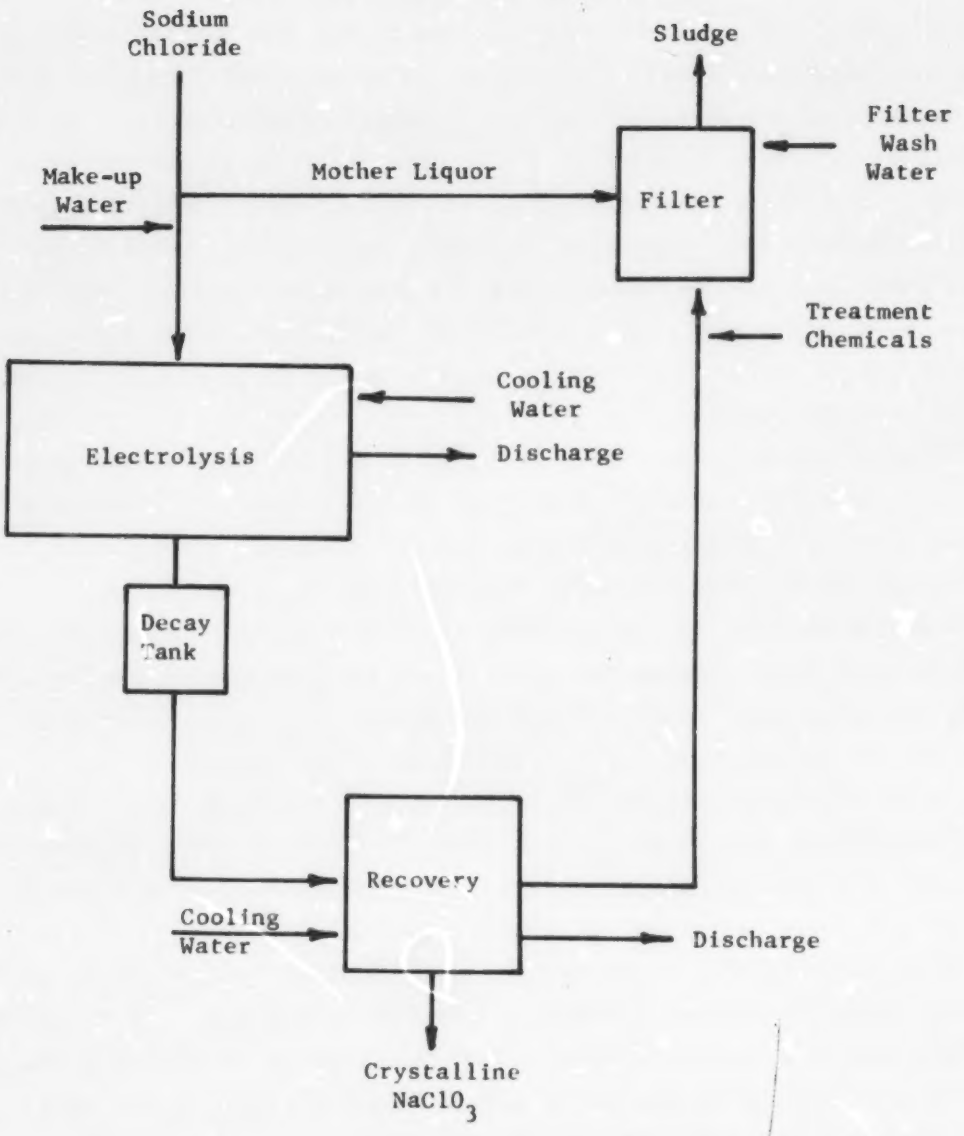

Figure 7. Sodium Chlorate Production Schematic

The sodium chlorate slurry is then centrifuged to separate the crystals from the mother liquor. The mother liquor is returned to the electrolytic cells, and the crystalline sodium chlorate dried in rotary driers. This completes the manufacturing process, and the product is loaded into drums or tank cars for shipping.

The primary wastewater discharged from sodium chlorate plants is uncontaminated cooling water, plus sludges formed through precipitation of rock salt impurities. Spills of mother liquor are fairly frequent, but are normally caught in spill sumps and returned to the process. Table 9 summarizes the raw wastewater properties for the three plants for which data were available. Plants 1 and 2 were visited during this study, and data for Plant 3 were taken from the permit application. Table 10 presents additional data on the discharge characteristics. Flows shown for Plants 1 and 3 represent total plant flows, including process lines other than sodium chlorate manufacture. The flow for Plant 2 is only for the sodium chlorate facility.

Plant 2 has developed and will implement a plant-wide pollution control plan involving total containment of all wastewaters, through a system of process changes, effluent reuse and evaporative ponds. A current and proposed water budget for the sodium chlorate process, only, is presented in Table 11. As a result of these process changes and reuse, Plant 2 anticipates a reduction in water use by 88 percent. Changes include separation and recycle of weak and strong effluents, elimination of once-through cooling water, and reduction in filter washwater.

There is little information on the specific nature of the effluent from the sodium chlorate facility at Plant 2. Data contained in Table 9 represent the combined plant discharge, of which the sodium chlorate discharge represents only about 30 percent. Current data are available, as presented in Table 12, on volume and sodium chloride content of the discharge. Based upon other information provided by the plant, it is estimated that the sodium chlorate discharge is on the order of 35 lbs/ton product.

In addition, there are two to three spills of mother liquor each year, totaling 20,000-30,000 gallons per spill. As a part of the

Table 9. Sodium Chlorate Effluent Character

Parameter	Plant 1		Plant 2		Plant 3		Range		Average	
	mg/l	lbs/ton prod.	mg/l	lbs/ton prod.	mg/l	lbs/ton prod.	mg/l	lbs/ton prod.	mg/l	lbs/ton prod.
BOD_5	12		NA		6.7		6.7-12.0		9.35	
		12.73		NA		8.52		8.52-12.73		10.63
TDS	240		3822		952		240-3822		1671.33	
		254.47		217.04		960.2		217.0-960.2		477.24
TSS	10		216		14		10-216		80.0	
		10.62		12.27		17.90		10.62-17.90		13.60
NH_3-N	1.5		7		6.8		1.5-7.0		5.10	
		1.59		0.40		8.69		0.40-8.69		3.56
Sulfate	25		1700		42.3		25-1700		589.1	
		26.47		96.59		54.08		26.47-96.59		59.05
Chloride	55		1200		276		55-1200		510.33	
		58.24		68.18		352.84		58.24-352.84		159.75
Barium	8		NA		NA		8		8	
		8.47		NA		NA		8.47		8.47

Table 9. (Continued)

Parameter	Plant 1		Plant 2		Plant 3		Range		Average	
	mg/l	lbs/ton prod.	mg/l	lbs/ton prod.	mg/l	lbs/ton prod.	mg/l	lbs/ton prod.	mg/l	lbs/ton prod.
Calcium	10		400		118		10-400		176.0	
		10.59		22.73		150.85		10.59-150.85		61.39
Sodium	100		1000		142		100-1000		414.0	
		105.88		56.82		181.53		56.82-181.53		114.74

Table 10. Sodium Chlorate Plant Discharge

Parameter	Plant 1	Plant 2	Plant 3
pH	6.0-8.0	6.0-10.0	6.4-7.3
Temperature, ^{o}F			
Winter	90	65	50
Summer	90	75	83
Flow, MG/ton Prod.	0.123	0.0023	0.150

Table 11. Sodium Chlorate Process Water Budget - Plant 2

	Present	Proposed
Evaporative Loss, MG/Yr.	6.0(1)	7.2(2)
Discharge, MG/Yr.	74.0	2.5(3)
Total Use, MG/Yr.	80.0	9.7

(1) Process evaporation
(2) Process + evaporative pond
(3) Reused elsewhere in plant

Table 12. Discharge Characteristics of Sodium Chlorate Plant 2

Flow, gal/day	191,000
NaCl Discharge, lbs/ton Product	11.0

Table 13. Anticipated Sodium Chlorate Plant Discharge to Evaporative Pond - Plant 2

	Flow gal/day	Concentration, mg/l
Flow	1,370	
NaCl		1,000
$NaClO_3$		3,000
$NaClO_4$		400
Na_2SO_4		1,400
$Na_2Cr_2O_7$		50
$CaCO_3$		500
Total Diss. Solids		6,350

Table 14. Cost of Sodium Chlorate Wastewater Control Program - Plant 2

Process Changes - Material	$56,000
Process Changes - Labor	27,000
Evaporative Pond* - Materials	12,000
Evaporative Pond* - Labor	2,000
Total Cost	$97,000

*1-acre lined pond

Plant 2 implementation plan, such spills will be caught and retained in evaporative ponds.

The anticipated sodium chlorate plant effluent from Plant 2, after in-plant modification, is shown in Table 13. This wastewater will flow to an evaporative pond, thus providing complete wastewater containment. The economics of the implementation plan, as estimated by Plant 2 for the sodium chlorate production line only, are summarized in Table 14. Evaporative ponds, together with process changes and recycle, appear to be a valuable and effective pollution control technique in those geographical regions where evaporation sufficiently exceeds rainfall to allow their use. A comparison of Figures 8 and 9 indicate that their use is essentially limited to the west and southwest regions of the country, however.

Sodium Borates

The plant visited produces monobor chlorate, a mixture of sodium metaborate and sodium chlorate. Monobor chlorate is manufactured by mixing caustic solution, borax and crystalline sodium chlorate. The reaction is exerthermic, and the resultant slurry is cooled on water-chilled rollers, to form flakes. The flakes are sized by screening. Dust (collected by bag collectors) and fines are returned to the continuous mixer. Oversized flakes are granulated, and returned to the screening operation. Figure 10 is a production schematic. The continuous mixer, chill rollers and granulator are cleaned by washing, once per shift.

There are two sources of process discharge from the plant; a continuous cooling water flow from the chill rollers, and cleanup water. The cooling water is non-contact once-thru well water. Based upon average operation, this cooling water flow constitutes 7200 gal/ton product. Cleanup water results from washing the mixer, granulator and chill rollers each shift. The quantity of water involved is 200-300 gal. per cleanup.

Both cooling and cleaning water are discharged to a common sewer of an adjacent industrial plant. This sewer is sampled only after

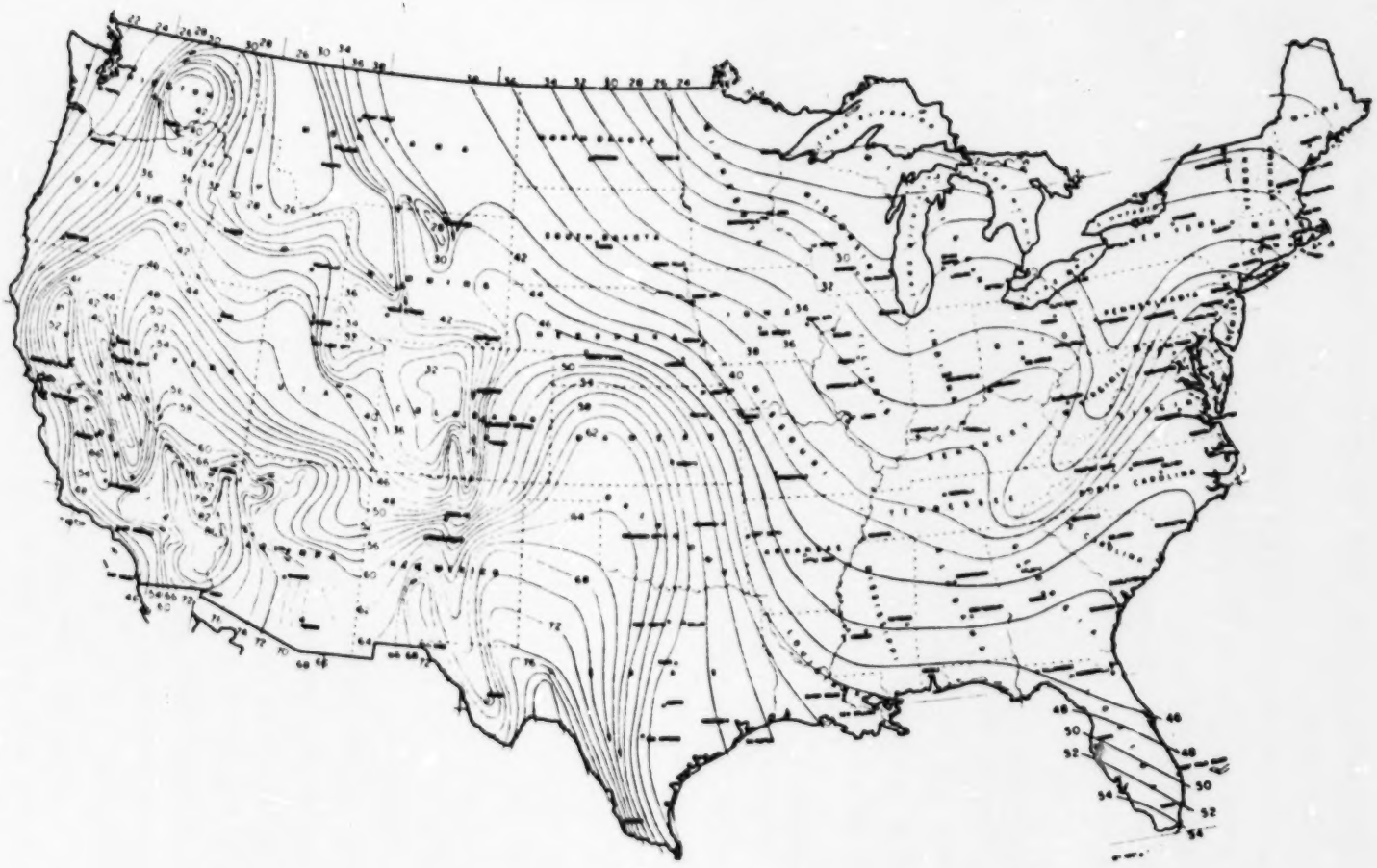

Figure 8. Mean Annual Inches of Lake Evaporation

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Figure 9. Mean Annual Inches of Precipitation

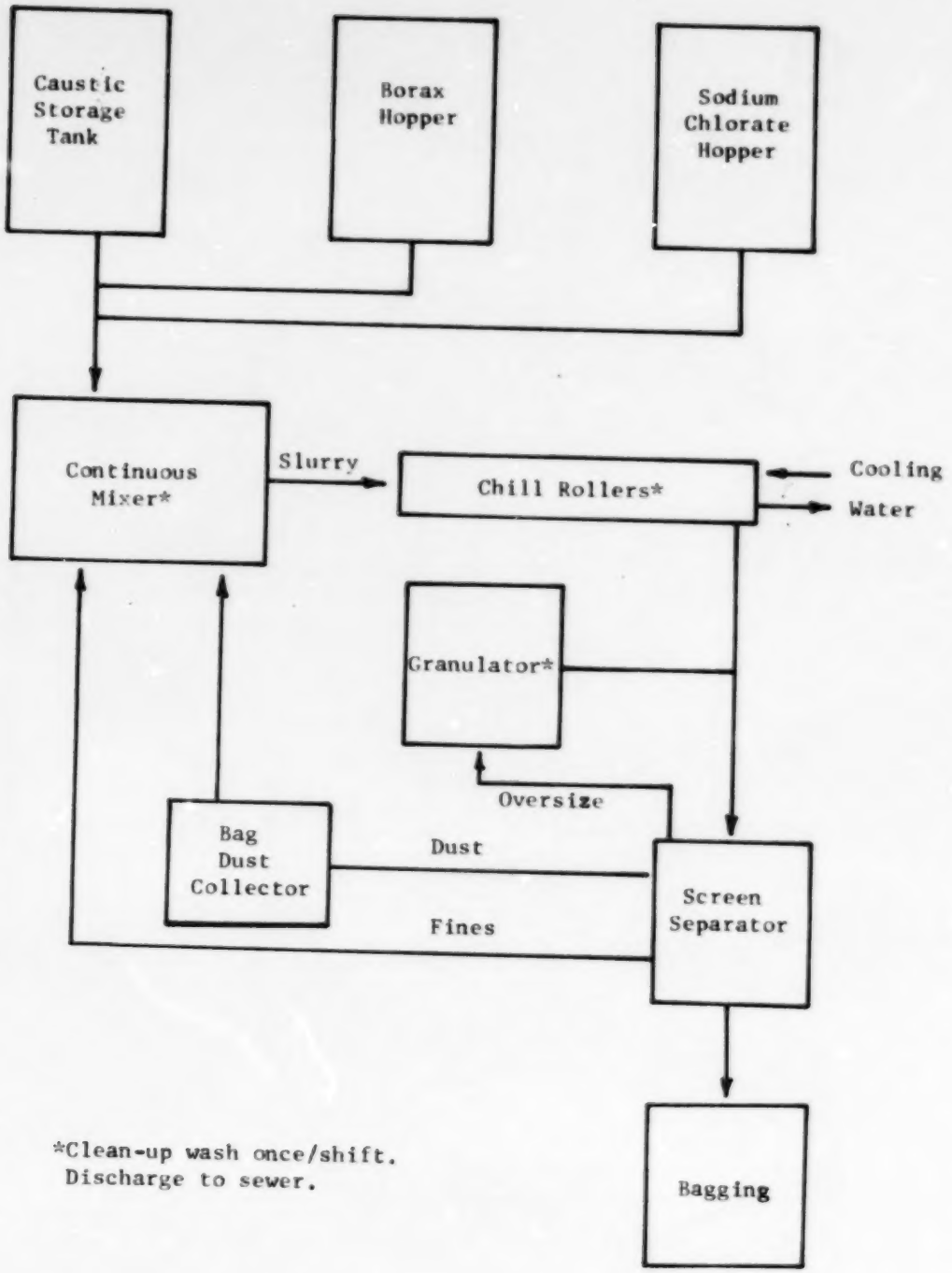

Figure 10. Monobor Chlorate Production Schematic

mixing of the two plants wastes. The combined flow of this sewer is 10.58 MGD. The borate process flow represents 1.36 percent of the total, with cleanup water being diluted (on an average daily basis) almost 500-fold by cooling water. The total sewer discharge consists of 99.9 percent cooling water and 0.1 percent combined process wastewater. Of the combined process (only) wastewater, the borate flow averages 22.7 percent of the total process flow. The wastewater will contain as industrial waste constituents sodium, chlorate and metaborate, and is expected to have a high pH. However, due to the high dilution factor, and batch (once/shift) discharge of borate wastewater it was not appropriate to extrapolate its character from data available on the combined discharge.

Sulfur

Bulk sulfur, brought in by hopper cars, is crushed by teethed rollers to 10 mesh size, and transported by conveyor belts to holding bins. Additional processing is shown in Figure 11. The crushed sulfur is placed, in charges of 750-800 lbs., into a batch mixer. Clay, if required, is added at 7-50 percent of the finished product. Wetting agents may also be added to allow field spraying of the pesticide as a liquid suspension.

After batch mixing, the preparation is conveyed to an enclosed grinding mill (Figure 12) to further reduce the size of the sulfur. In order to prevent explosions, an oxygen-lean atmosphere must be maintained in the grinding mill. This is accomplished by using CO_2 rich flue gas from the plant steam boiler. After grinding, the mixture goes to a final post-blender, and then is bagged for shipment.

When shifting from one product to another, it is necessary to clean out the mix and grinding system. As a first step, the caked material in the units is chipped out by hand. Then,charges of clay are run through the batch mixer, grinding mill and post-blender. This clay is stockpiled, and later used when the same product is again being formulated.

Plant wastes include sanitary sewage, shower drainage, laundry

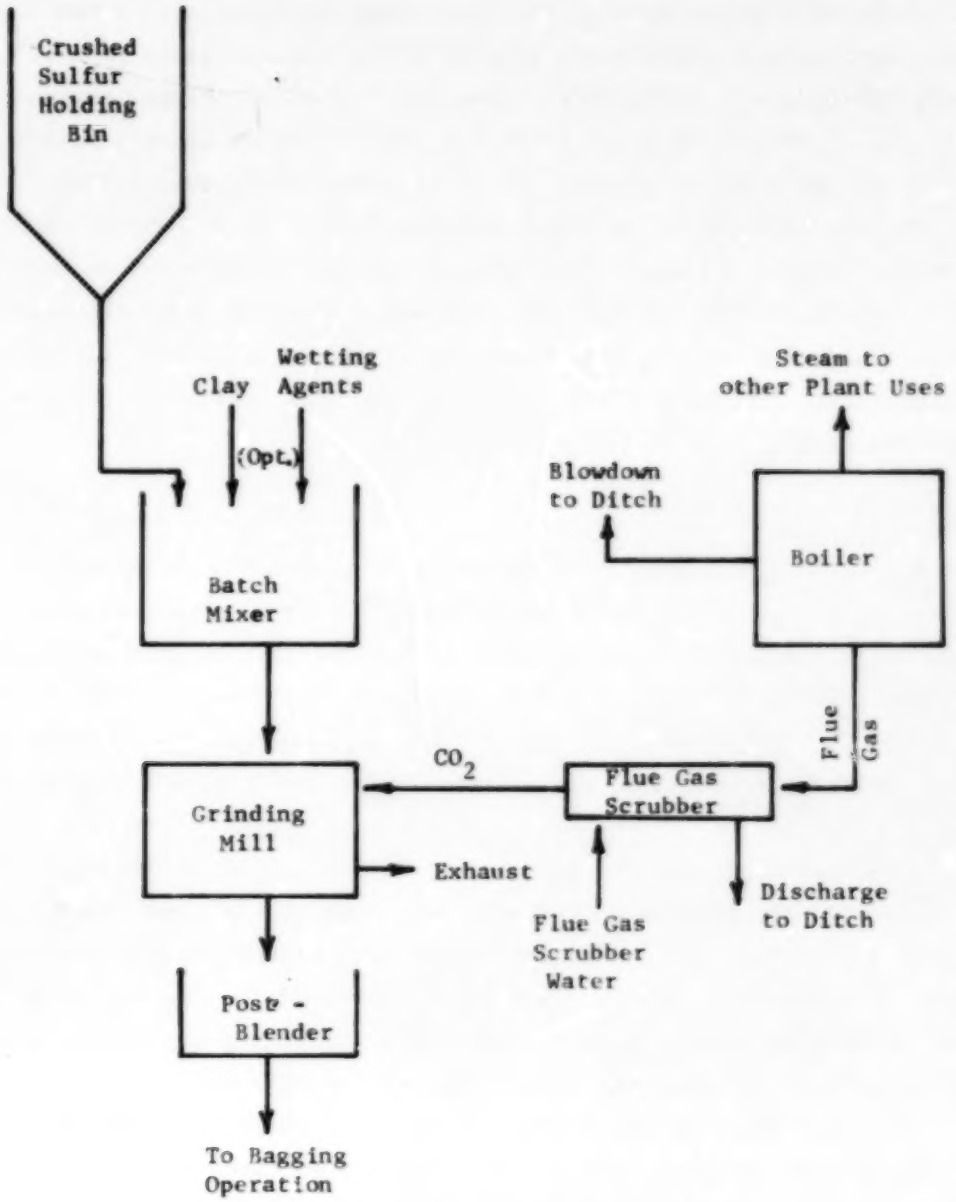

Figure 11. Sulfur Pesticide Production

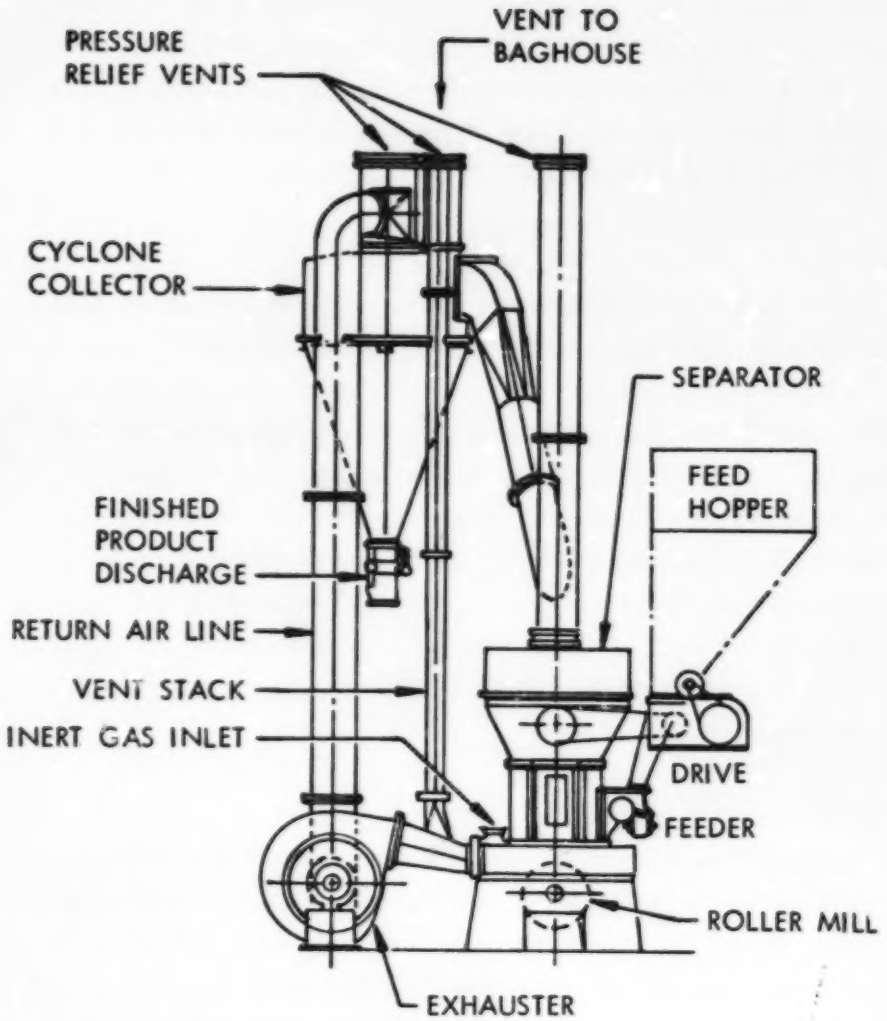

Figure 12. Typical Sulfur Grinding Unit (6)

wastewaters, gas scrubber water and boiler blowdown (see Figure 11). All sanitary waste including shower and laundry discharges, go to a company-owned septic tank. Gas scrubber water, estimated at 250,000 gal/month, and boiler blowdown (twice/year discharge) flow to an open ditch and thence into a roadside drainage ditch. The company is under the impression that a discharge permit is not required, and has therefore not submitted an application. No information is available on the character of the boiler blowdown or gas scrubber cooling water. With the exception of these two product-associated processes, there is no wastewater involved in production.

Zinc Sulfate

Basic zinc sulfate is manufactured by first adding metallic zinc to concentrated sulfuric acid, to form zinc sulfate solution. Lime is then added to neutralize, and the precipitate slurry is decanted by pipe into drum driers. Water vapor from the driers is collected and vented to stacks. Cleanup water from the batch mix vats is either saved to mix with the next batch, or evaporated in the drum driers to recover product. As a result of the processing methodology employed at this plant, there is no wastewater effluent associated with the manufacture of zinc sulfate. All product spills are caught in spillpans below each processing unit. Spilled liquids are recycled back into the processing line.

General Problems

Among producers of inorganic pesticides, one problem appears common. This relates to the cleanup of returnable containers used to ship their products. Normally, these are drums or tank cars, and to avoid contamination from shipment of one product to the next, cleanup procedures are required. In those plants which already have a wastewater associated with their manufacturing process, container cleanup water is added to other plant effluents, and handled as a part of that flow.

However, one major inorganic pesticide manufacture of heavy metal products has recently completed a process modification program which

has eliminated all process-associated wastewaters. The major pollutional concern remaining is how to clean out and reuse the 55-gallon drums in which they ship their products, without producing difficult-to-treat wastewaters. This problem has not been resolved, and several thousand used drums are currently stockpiled in a storage yard, awaiting the development of a cleanup procedure which will avoid the generation of wastewater.

VII. POLLUTION CONTROL TECHNOLOGY

Seven of the eleven inorganic pesticides investigated in this study had no effluent associated with their manufacturer, as a result of the specific production technology used. These seven are,

- arsenic acid
- calcium arsenate
- copper sulfate
- lead arsenate
- sodium arsenite
- sulfur
- zinc sulfate

The remaining four did have wastewaters, ranging from predominantly cooling water (sodium chlorate and sodium borate) to complex process waste effluent (copper carbonate and tri-basic copper sulfate). One sodium chlorate plant has developed a program for zero effluent, based upon extensive process changes, recycle and discharge to an evaporative pond.

Of the six sodium chlorate plants identified in this study (Table 4), three are located in the south, one in the southwest, one in the northwest and one in the northeast. A comparison of annual evaporative (Figure 8) and annual rainfall (Figure 9) reveals that use of evaporative ponds is only feasible for that plant located in the southwest. For all other locations, rainfall equals or exceeds evaporation.

However, one plant also plans to implement in-plant process controls, which will greatly reduce mass pollutant discharge. Select data from Table 13, as compared with current discharge levels (Table 9) are presented in Table 15. The implementation of process controls will thus reduce mass pollutant discharges in excess of 99 percent. At the subject plant, this residual effluent will discharge to an evaporative pond.

Effluent from the copper carbonate facility (Table 7) is high in copper (13 mg/l), and dissolved and suspended solids. In addition, it contains 0.62 lbs. of other heavy metals per ton of product, due to impurities in the copper used. Of particular significance is the lead (0.7 mg/l) and zinc (1.3 mg/l) in the effluent. Plans to install a

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Table 15. Effect of In-Plant Controls an Mass Pollutant Discharge

Parameter	Current		Proposed	
	mg/l	lbs/ton prod.	mg/l	lbs/ton prod.
Sodium	1000	56.8	1579	0.49
Calcium	400	22.7	200	0.06
Sulfate	1700	96.6	946	0.30
Chloride	1200	68.2	607	0.19
Tot. Diss. Solids	3822	217.0	6,350	1.99

Table 16. Comparison of Copper Carbonate and TBCS Effluent Concentrations

Parameter	$CuCO_3$, mg/l	TBCS, mg/l
pH	6.5	6.4
Copper	13	136
Iron	3.6	38
Magnesium	1.0	1.5
Manganese	0.1	0.17
Nickel	0.1	0.9
Lead	0.7	0.12
Zinc	1.3	1.4
NH_3-N	10	4,800

precipitation treatment system at this plant are now under development. Based upon data developed by Patterson and Minear (11) in an extensive study of treatment technology for pollution control, precipitation treatment appears most applicable for this waste. By proper pH control and efficient solids removal, copper should be reduced to 0.2-0.5 mg/l in the process wastewater. Assuming no process changes to reduce total effluent flow, this would result in a copper discharge of 0.02-0.05 lbs/ton product, or a reduction of 96 to 98 percent. Effluent levels for lead and zinc, based upon the same report, should be reduced to 0.02-0.20 and 0.1-0.5 mg/l respectively, depending upon the efficiency of solids removal (11).

Treatment of the tri-basic copper sulfate waste is also proposed, by the plant manufacturing that product. However, treatment of this waste is more difficult then the copper carbonate waste, due to the presence of ammonia which acts as a complexing agent to prevent effective precipitation. The ammonia results from the addition of ammonium hydroxide to copper sulfate solution, to form the tri-basic copper sulfate. The pH values of the effluent from both the copper carbonate and tri-basic copper sulfate are comparable, and except for complexation effects, the heavy metal solubility (and therefore effluent metal levels) would be expected to be similar. This is not true, as shown in Table 16. Data from Table 16 is extracted from Tables 7 and 8.

Ammonia-nitrogen is present in the TBCS effluent at 4800 mg/l. Although not as strong a complexing agent as for example cyanide, at that concentration ammonia does exert a significant effect upon residual metal solubilities. Copper, iron and nickel levels are up to ten times greater in the TBCS effluent, while other metals are comparable to the copper carbonate wastewater. In order to effectively treat this waste, the ammonia must be removed. Two alternatives are (1) to replace the ammonia hydroxide by some other base in the process, or (2) remove the ammonia from the wastewater prior to metal precipitation. The plant having this wastewater is currently assessing methods of pollution control. However, they feel that it is not feasible to substitute another base for the ammonium hydroxide, and are currently investigating the

possibility of stripping the ammonia from solution prior to heavy metal precipitation. This potentially creates an air pollution problem.

In summary, with the exception of the complexation problem for TBCS wastewater, pollution problems associated with all of the inorganic pesticides of this study are either non-existent, or greatly alleviated by in-plant modifications and/or implementation of well established treatment technology. A caution must be observed relative to those products which, in this study, exhibited no discharge. Each of the seven products is manufactured by two or more producers, and it was only at the specific plants visited that zero effluent was observed. It is probable that other producers may, in fact, have wastewaters associated with their manufacture of these products and, at least for lead arsenate, quite likely. However, the studies reported here demonstrate that process technology is available and currently in use to achieve zero effluent for those seven products.

VIII. ACKNOWLEDGEMENTS

The cooperation of E. Martin and D. Becker of the Effluent Guidelines Division, and personnel the Regional Offices of the Environmental Protection Agency, the Manufacturing Chemists Association and the National Agricultural Chemicals Association greatly assisted the performance of this study.

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Appendix A

Companies Contacted on Inorganic Pesticides

Allied Chemical	P.O. Box 2120 Houston, Texas 77001
American Cyanamid Company	P.O. Box 400 Princeton, New Jersey 08540
American Smelting and Refining Company	120 Broadway New York, New York 10005
Amvac Chemical Corporation	4100 E. Washington Blvd. Los Angeles, California 90023
Anaconda American Brass Company	P.O. Box 747 Waterbury, Connecticut 06720
Apache Chemicals, Inc.	P.O. Box 17 Rockford, Illinois 61105
Chem Met. Corporation	10 E. Erie Street Chicago, Illinois 60611
Chemetron Corporation	1250 Terminal Tower Cleveland, Ohio 44113
Chempar Chemical Company	260 Madison Avenue New York, New York 10016
Chemtech Corporation	7882 Folk Avenue St. Louis, Missouri 63143
Chevron Chemical Company	200 Bush Street San Francisco, California 94120
Cities Service Company	3445 Peachtree Road, N.E. Atlanta, Georgia
Diamond Shamrock Chemical Company	1100 Superior Avenue Celveland, Ohio 44114
Dow Chemical Company	200 Main Street Midland, Michigan 48640
Filo Color and Chemical Corporation	347 Madison Avenue New York, New York 10017
FMC Corporation	100 Niagra Street Middleport, New York 14105

Freeport Minerals Company	161 East 42 Street New York, New York 10017
Great Lakes Chemical Corporation	P.O. Box 2200, Hwy. 52 N.W. West Lafayette, Indiana 47906
The Harshaw Chemical Company	1945 East 97th Street Cleveland, Ohio 44106
Hooker Electrochemical Division	Niagara Falls, New York 14302
Kerr-McGee Chemical Corporation	Kerr-McGee Center Oklahoma City, Oklahoma 73102
Lobel Chemical Company	100 Church Street New York, New York 10007
Los Angeles Chemical Company	4545 Ardine Street South Gate, California 90280
Mallinckrodt	Second & Mallinckrodt Streets St. Louis, Mo. 63160
Merck & Company	126 E. Lincoln Avenue Rahway, New Jersey 07065
Nor-Am Agricultural Products, Inc.	20 N. Wacker Drive Chicago, Illinois 60606
Olin Corporation	120 Long Ridge Road Stamford, Connecticut 06904
Pennwalt Corporation	1713 S. California Avenue Monrovia, California 91016
Phelps Dodge Refining Corporation	300 Park Avenue New York, New York 10022
PPG Industries, Inc.	New Albany Road Moorestown, New Jersey 08057
Rhodia Inc., Chipman Div.	120 Jersey Avenue New Brunswick, New Jersey 08903
Rohm and Haas Company	Independence Mall West Philadelphia, Pa. 19105
Rona Pearl Company	E. 21st & 22nd Street Bayonne, New Jersey 07002

The Shepherd Chemical Company	5000 Poplar Street Cincinnati, Ohio 45212
Southern California Chemical Co., Inc.	8851 Dice Road Santa Fe Springs, California 90670
Stauffer Chemical Company	Westport, Connecticut 06880
Tenneco Chemicals	Turner Place, P.O. Box 2 Piscataway, New Jersey 08854
Texas Gulf, Inc.	200 Park Avenue New York, New York 10017
Triangle Chemical Company	P.O. Box 4528 Macon, Georgia 31208
U.S. Borax & Chem Company	3075 Wilshire Blvd. Los Angeles, California 90005
United Chemicals Company	401 Delaware Kansas City, Missouri
Van Waters & Rogers	Box 3200 San Francisco, California 94119
Ventron Corporation	2400 Congress Street Beverly, Mass. 01915
Vineland Chemical Co., Inc.	P.O. Box 745 Vineland, New Jersey 08360
Vistron Corporation	Midland Building Cleveland, Ohio 44115
Volunteer Purchasing Groups, Inc.	P.O. Box 460 Bonham, Texas 75418
W. A. Cleary Corporation	P.O. Box 749 New Brunswick, New Jersey 08903
Woolfolk Chemical Works, Ltd.	Fort Valley, Georgia 31030

APPENDIX B

Metric Conversion Factors

English Unit		Metric Equivalent
lb.	=	0.454 kg
ton	=	0.908 kkg
gal.	=	3.785 liters
	=	3.785×10^{-3} meters^3
MG	=	3.785×10^{6} liters
	=	3.785×10^{3} meters^3
lbs/ton	=	0.500 kg/kkg
lbs/MG	=	0.120 mg/l
	=	0.120×10^{-3} kg/m^3